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Anticorrosion properties of pigments based on ferrite coated zinc particles

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Abstract

The paper deals with a new anticorrosion pigment, synthesized on a core-shell basis. For its syntheses a starting substance is used that forms the lamellar shaped core; namely lamellar zinc. The cover of the core is represented by zinc oxide, which is in fact partly oxidized lamellar zinc core, and is created during the calcination of the pigment. The compound that forms the top layer of the core, a ferrite, is also formed during calcination.

The formula for the prepared pigment is then defined as $Me_xZn_{1-x}Fe_2O_4/Zn$ and the formula of thin ferrite layer is $Me_xZn_{1-x}Fe_2O_4$ (where Me = Ca, Mg). Due to its shape, this anticorrosion pigment includes another anticorrosion effect, the so called "barrier effect". The mechanisms of anticorrosion effect, corrosion efficiency and mechanical properties were investigated for epoxy-ester paint systems with 10%pigment volume concentration (PVC). Mechanical tests were performed to determine the adhesiveness and mechanical resistance of paints and accelerated corrosion tests were carried out to evaluate efficiency against chemical degradation factors.

Keywords: Anticorrosion pigment, core-shell, lamellar ferrite, zinc

1. Introduction

The most widespread protection of metal materials is the application of organic coatings created from anticorrosion paints. This method secures the chemical or electrochemical reaction of an anticorrosion pigment with a metal alone or with a corrosive agent penetrating through the protective organic coating. Some of the commonly used pigments in such paints are zinc and various ferrite compounds. As zinc and especially zinc oxide is very suitable to be mixed with other pigments, development in the area of these pigments is focused to test anticorrosion properties of compound pigments and mixtures of pigments

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[1,2]. The aim of pigment mixtures development is to enhance the anticorrosion efficiency of non-toxic pigments and shift its efficiency closer to the old, toxic (but very efficient) chromate and lead pigments. Such development is necessary to meet tough environmental norms that are getting more and more strict [3,4]. The latest EU legislation on organic coatings took effect in 2010 and was aimed at reducing volatile organic compounds in paint systems [3].

The intention is to develop a pigment combining several anticorrosion mechanisms, e.g. mechanical, electrochemical or chemical. There have been intensive efforts focused on the barrier mechanism and the barrier effect of newly developed core-shell pigments and core-shell pigments with lamellar particle shapes [5,6,7,8,9,10]. During the drying of these paint films, the lamellar particles of the pigment occupy a position parallel to the base. Due to this orientation, they contribute to the improvement of the film's mechanical properties and prevent the direct penetration of humidity, oxygen, and aggressive ions towards the base. The appropriate placement and reinforcement of non-isometric pigment particles in the paint film prolongs the penetration of gas and vapor diffusion to more than 10 times the thickness of the film and retards corrosion [11]. Today, just one mechanism is not enough; therefore a combination of several effects is essential.

A ferrite with an anticorrosion mechanism based on passivation of metal surface [12,13,14,15,16,17], by forming non-soluble compounds [18], seems to be a promising partner with zinc, which has very strong anticorrosion properties at certain conditions [19]. But the electrochemical effect of zinc won't be the major one. In this pigment, the electrochemical effect of zinc oxide is strongly diminished as a result of oxidation, low conductive ferrite presence [20] and insufficient PVC to secure conductivity in whole pigmented area. On the other hand, our new pigment benefits by zinc oxide properties. Thanks to ZnO basic character, it reacts with carboxyl groups and forms soaps with suitable binders, shifts pH to basic values which are not very hostile to corrosion reactions and can be mixed with other pigments with no limitations. It offers very interesting optical properties, very good hiding power, a refractive index value of 2.03 and also speeds up the paint drying process during oxypolymerization of binders.

To contribute to the research on compound pigments, the paper presents anticorrosion pigments synthesized on a core-shell basis. The focus of the work is to point in the direction of developing a non-toxic anticorrosion pigment that combines more anticorrosion mechanisms and also not be so difficult to synthesize.

2. Experimental

2.1. Calcination of magnetite, zinc and carbonate

The used pigment synthesis route is based on modifying lamellar shaped zinc dust particles (Benda-Lutz® Zinc Powder Flakes Z 2012) by reaction with iron oxide and another oxide of alkaline earth metals (Mg or Ca). Table 1 illustrates percentages by weight of starting materials. On the surface of the zinc particles that oxidize easily, a thin layer of zinc oxide is formed, due to heat applied during the calcination process. The second layer is later bonded to this oxidized surface. The second layer is composed of hematite or other ferrite layers of different composition, depending on a cation type of starting substances. In general, ferrites are groups of spinel lattice compounds that include trivalent ferrite cations, which are combined with suitable bi and trivalent cations within a cubic structure. Magnetite is used as the best iron ion source along with bivalent cations Mg^{2+}, Ca^{2+} which are the best for spinel cubic structure build thanks to their atomic ratio. Zn^{2+} cations can also nicely form the structure.

We found that the intended product was created in short calcination times at 400°C. For example, the zinc core, which is oxidized on the surface for ZnO, forms with Fe_3O_4 at 400°C for 30 minutes $ZnFe_2O_4$/Zn. Prepared pigment properties were determined to allow presuming applicability in the polymer binders, as well as anticorrosion efficiency.

Optimal PVC was selected to keep the exclusive mechanical properties of the final paint, as epoxy-ester binder was chosen. Prepared pigments were then dispersed into this binder and the paints applied to corrosion test panels. A series of accelerated anticorrosion test were carried out and the results compared with isometric particle ferrites and commercially produced Bayferrox 120 pigment.

Table 1. Percentages by weight of starting materials

Pigment	**Zn**	**ZnO**	**α-Fe_2O_3**	**Fe_3O_4**	**$CaCO_3$**	**$MgCO_3$**
	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
$ZnFe_2O_4$/Zn	79,4	7,9	0	12,7	0	0
$ZnFe_2O_4$/Zn	79,4	7,9	12,7	0	0	0
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn	78,3	7,8	0	12,5	0	1,4
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn	78,3	7,8	12,5	0	0	1,3
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn	78,1	7,8	0	12,5	1,6	0
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn	78,1	7,8	12,5	0	1,6	0
$MgFe_2O_4$/Zn	72,4	7,9	0	12,7	0	6,9
$MgFe_2O_4$/Zn	72,7	7,9	12,7	0	0	6,7

2.2. Properties of pigments

2.2.1 Specific mass [21,22] Specific mass was determined by a gas pycnometer AutoPycnometer 1320 (Micrometrics Instrument Corp., USA).

2.2.2. Oil absorption [21,22] Sorption of linseed oil (the amount of linseed oil in grams necessary for creating a paste with pre-defined properties from 100 g of the pigment) was determined by the mortar–pestle method. The specific mass and oil consumption determination is important for the calculation of the critical pigment volume concentration (*CPVC*) and for the formulation of paints [21].

2.2.3. pH of aqueous extracts [21,22] The procedure for determining the pH value of the aqueous extract was derived from standard ISO 789-9. 10% pigment suspensions were prepared in redistilled water and allowed to stand for 28 days at a constant temperature.

2.2.4. Particle morphology [21,22] The surface and the shape of the pigment particles were examined using an SEM (scanning electron microscope) JEOL-JSM 5600 LV (Japan).

2.2.5. X-ray diffraction analysis (XRD) [21,22] patterns were measured with a Diffractometer D8 Advance (Bruker AXS).

2.2.6. Formulation of paint with the tested pigments

To identify the effect of the formulated pigments on the anticorrosion efficiency, the coated pigments were dispersed in epoxy-ester resin (*EPOXYESTER (CHS EPOXY 101 X60,* Spolchemie a.s., Czech Republic**)**). The pigment volume concentration was 10%. Using titanium dioxide (*Pretiox® AV 01*, *Precheza a.s.,Czech Republic*), the pigment volume concentration in paints was optimized to a constant *PVC/CPVC* ratio of 0.35.

2.2.7. Binder characteristics: solvent based epoxy–ester binder (60 % solution of high molecular weight epoxide resin esterified by dehydrated castor and soya oil); Dry matter: 58-62 %; Solvent: xylene

2.2.8. Inert pigment characteristics: titanium white (TiO_2 anatase type); Density: 4.64 $g.cm^{-3}$; Oil consumption: 26 g/100 g of the pigment

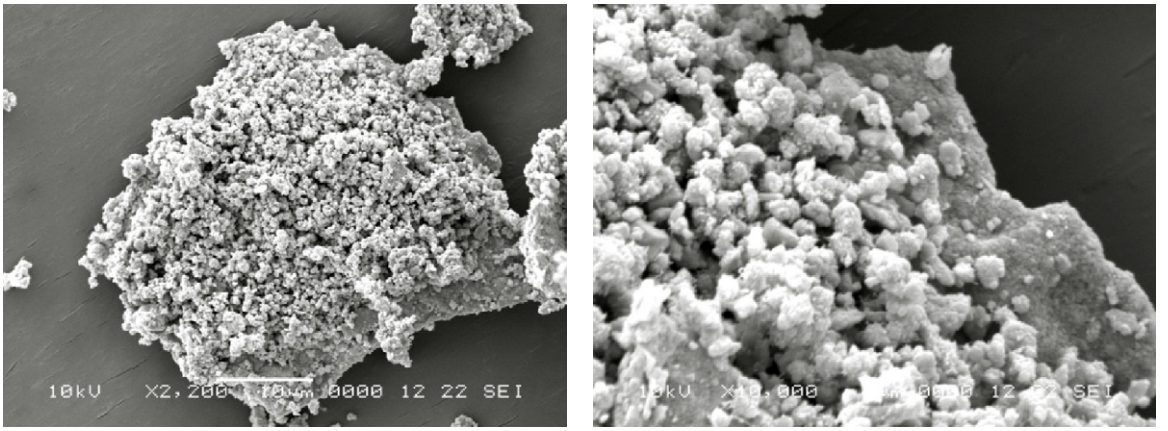

Fig. 1. (a, b) SEM micrograph of $ZnFe_2O_4$/Zn (zoom 2, 200x and 10, 000x, taken by authors at the Faculty of Chemical Technology, University of Pardubice, instrument from chapter 2.2.4)

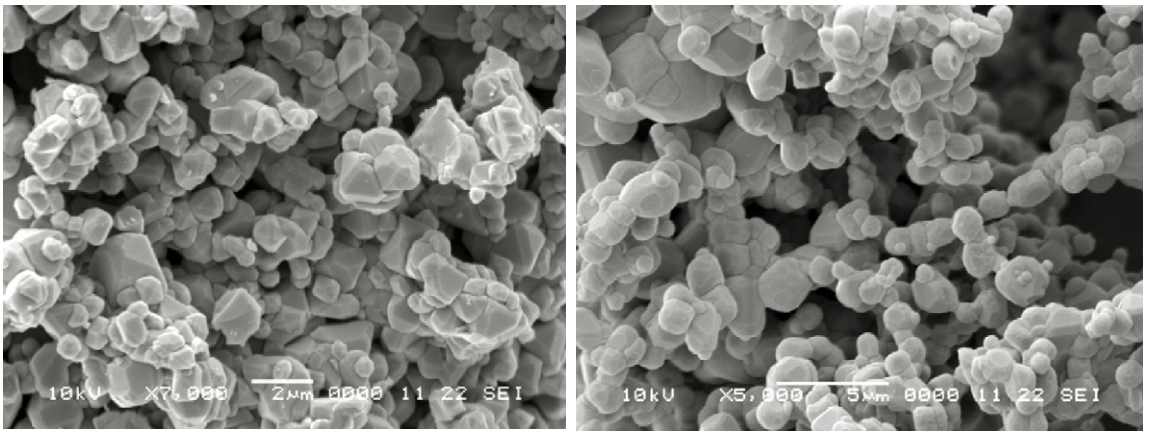

Fig. 2. (a) SEM micrograph of $Mg_{0.2}Zn_{0.8}Fe_2O_4$ (b) SEM micrograph of $MgFe_2O_4$ (zoom 7, 000x and 5, 000x, taken by authors at the Faculty of Chemical Technology, University of Padubice, instrument from chapter 2.2.4)

2.3. Anticorrosion efficiency of the prepared pigments

A practical observation of anticorrosion properties was carried out according to standardized accelerated cyclic corrosion tests. The paints were exposed at a higher rate to a corrosion agent (chloride ions, water condensation or sulphur dioxide) that simulated one of the specific corrosion environments. Accelerated corrosion tests were carried out with water condensation [23,24], the accelerated cyclic corrosion test in the atmosphere of NaCl with water condensation [23,24,25,26] and the accelerated cyclic corrosion test in the atmosphere of SO_2 with water condensation [23,24,25]. The coatings were removed from the tested samples after 2, 100 h of exposure and corroded surfaces were evaluated.

After exposure to corrosion tests, the paints were evaluated by methods derived from ASTM D 714-87, ASTM (American Society for Testing and Materials) D 610 and ASTM D 1654-92 standards [6,21,23,24,27]. By transforming the results of the corrosion changes to a point scale (100-0, 100 being the highest value and 0 the lowest) and by arranging these numerical values in a mathematical relation (1), the overall anticorrosion efficiency of the pigmented coating was identified. The overall anticorrosion efficiency - Ae was calculated as the arithmetic mean of three evaluated parameters (degree of surface corrosion A_1, degree of blistering A_2 and corrosion in a scratch A_3) [2,21,23,24,27]. The degree of surface corrosion and the degree of blistering were assessed by visual comparison. The comparison was made to the graphical ASTM standard model. Scratch corrosion was calculated as an average distance value of corrosion damage on both sides from the scratch.

$$Ae = \frac{A_1+A_2+A_3}{3} \quad (1)$$

2.4. Corrosion test with water condensation

This corrosion test took place in a condenser chamber with distilled water condensation. During this test all samples were exposed to the nonstop effect of condensing distilled water at 38°C. The samples were evaluated after 2, 100 h of exposure.

2.5. Cyclic corrosion test with NaCl mist and humidity condensation (ČSN ISO 9227)

This cyclic corrosion test took place in a condenser chamber with salt mist. During this test, corrosion processes were accelerated by the action of condensed humidity and NaCl at an increased temperature (35±1°C). The 12-h cycle was divided into three parts: 6 h of sample exposure to salt mist (5% solution of NaCl) at a temperature of 35±1°C, 2 h of exposure at a temperature of 23°C, and 4 h of distilled water condensation at a temperature of 40°C. The samples were evaluated after 2, 100 h of exposure. To prove their anticorrosion efficiency in this test, the pigments in the paint must display their ability to protect against the corrosive effects of NaCl as well as increased humidity.

2.6. Cyclic corrosion test in the presence of condensed H_2O and SO_2 (ČSN ISO 6988)

This cyclic corrosion test took place in the SO_2 environment in a condenser chamber. Corrosion processes were accelerated in the hermetically sealed chamber with the effect of condensing humidity and SO_2 vapours (where 1 dm^3 of SO_2 acts in a 100 dm^3 chamber for 8 h). The test was completed in accordance with ISO 6988. Exposure to the corrosive environment took place in 24-h cycles: 8 h of water condensation at 36°C with the SO_2 content and 16 h of drying at 23°C. The samples were evaluated after 2, 100 h of exposure. To prove their anticorrosion efficiency in this test, the pigments in the paint must display their ability to protect against the corrosive effects of SO_2 and against the acidic condensed humidity at an increased temperature.

3. Results

3.1. Properties of the pigment particles

Final pH values of aqueous suspensions of isometric ferrites were ranged from 6.9 to 9.6. The pH factor of core-shell ferrites was ranged from 7.2 to 9.6.

Table 2. Pigments characterization

Pigment	Morphology of particles	CPVC (%)	pH[28]
$ZnFe_2O_4$	Isometric	43,30	6,9
$Ca_{0,2}Zn_{0,8}Fe_2O_4$	Isometric	49,96	9,6
$Mg_{0,2}Zn_{0,8}Fe_2O_4$	Isometric	51,04	8,1

$MgFe_2O_4$	Isometric	45,06	8,3
$ZnFe_2O_4$/Zn (magnetite)	Lamellar	43,06	7,2
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	Lamellar	47,14	8,6
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	Lamellar	42,43	8,8
$MgFe_2O_4$/Zn (magnetite)	Lamellar	37,55	9,6
Fe_2O_3 (Bayferrox 120)	Isometric	40,00	5,7

3.2. Determination of anticorrosion efficiency in an environment of condensed humidity

Corrosion on the scratch was less developed with isometric particle ferrites than the scratch corrosion with core-shell. Core-shell ferrites have better resistance against blistering and also show higher overall anticorrosion efficiency. Core-shell ferrites arrangement in the order of their anticorrosion efficiency: $Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn = $MgFe_2O_4$/Zn > $Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn > $ZnFe_2O_4$/Zn.

Table 3. Corrosion evaluation – after 2, 100 h in an environment of condensed humidity

Pigment	**Blisters**	**Surface corrosion**	**Corrosion on a scratch**	**Overall anticorrosion efficiency**
	Valuating No.	Valuating No.	Valuating No.	
$ZnFe_2O_4$	60	0	90	50
$Ca_{0,2}Zn_{0,8}Fe_2O_4$	75	95	90	87
$Mg_{0,2}Zn_{0,8}Fe_2O_4$	60	0	90	50
$MgFe_2O_4$	75	80	80	78
$ZnFe_2O_4$/Zn (magnetite)	100	80	80	87
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	95	70	88
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	95	80	92
$MgFe_2O_4$/Zn (magnetite)	100	95	80	92
Fe_2O_3 (Bayferrox 120)	75	60	80	72

3.3. Determination of anticorrosion efficiency in an environment of NaCl and condensed humidity

Both dimensional pigment types had similar results in scratch corrosion. The core-shell ferrites, prepared from magnetite starting substance, increased anticorrosion properties in contrast to those synthesized from hematite.

Table 4. Corrosion evaluation – after 2, 100 h in an environment of NaCl and condensed humidity

Pigment	Blisters	Surface corrosion	Corrosion on a scratch	Overal anticorrosion efficiency
	Valuating No.	Valuating No.	Valuating No.	
$ZnFe_2O_4$	75	60	90	75
$Ca_{0,2}Zn_{0,8}Fe_2O_4$	100	95	90	95
$Mg_{0,2}Zn_{0,8}Fe_2O_4$	75	60	90	75
$MgFe_2O_4$	100	95	90	95
$ZnFe_2O_4$/Zn (magnetite)	100	80	90	90
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	80	90	90
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	80	90	90
$MgFe_2O_4$/Zn (magnetite)	100	70	90	87
Fe_2O_3 (Bayferrox 120)	100	80	90	90

3.4. Determination of anticorrosion efficiency in an environment of SO_2 and condensed humidity

Isometric ferrites are more susceptible to scratch corrosion, compared to core-shell. The core-shell ferrites increase a coating's resistance to blistering, protection of metal surface and inhibit corrosion on scratch. Significantly better anticorrosion properties of core-shell ferrites are given by higher solubility of zinc and zinc oxide in an acid environment [7]. Core-shell ferrite arrangement in the order of overall anticorrosion efficiency: $Mg_{0,2}Zn_{0,8}Fe_2O_4/Zn \geq Ca_{0,2}Zn_{0,8}Fe_2O_4/Zn > ZnFe_2O_4/Zn > MgFe_2O_4/Zn$.

Table 5. Corrosion evaluation: after 2, 100 h in an environment of sulphur dioxide and condensed humidity

Pigment	Blisters	Surface corrosion	Corrosion on a scratch	Overall anticorrosion efficiency
	Valuating No.	Valuating No.	Valuating No.	
$ZnFe_2O_4$	75	0	50	42
$Ca_{0,2}Zn_{0,8}Fe_2O_4$	75	90	50	72
$Mg_{0,2}Zn_{0,8}Fe_2O_4$	75	20	50	48
$MgFe_2O_4$	75	90	50	72
$ZnFe_2O_4$/Zn (magnetite)	100	95	70	88
$Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	95	80	92
$Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn (magnetite)	100	90	80	90
$MgFe_2O_4$/Zn (magnetite)	100	70	70	80
Fe_2O_3 (Bayferrox 120)	75	70	50	65

4. Discussion

4.1. Properties of the pigment particles

The results confirmed that the desired products were synthesized. All three phases - zinc, zinkite and franklinite were present in all samples of pigment. According to the results from XRD analysis, the core-shell ferrites prepared from magnetite form a better product, containing no unwanted crystal phases. Such unwanted phases indicate the presence of alloys in the samples prepared from hematite. In the case of compound pigments, only the franklinite $ZnFe_2O_4$ was detected. Nevertheless, the Mg and Ca ions were also included in the franklinite spinel lattice and were imbedded into the lattice by isomorphic substitution. The SEM images of tested pigments revealed that the lamellar morphology of the particles was unchanged by coating (Fig. 1). The pH values of the suspension of the coated pigments were basic and thus suitable to form soaps with carboxyl groups present on binder chains. Only the pH values of the $ZnFe_2O_4$/Zn pigment suspensions were mildly basic.

4.2. The overall evaluation and comparison of degradation in particular chambers

Table 3-5. illustrates the corrosion evaluation after 2, 100 hours of exposure. The core-shell pigments proved better in anticorrosion efficiency. This is perfectly clear when studying the test results obtained in the water humidity chamber and in the chamber with sulphur dioxide and water humidity. When focused on starting substances, the core-shell pigments synthesized from magnetite showed better results than pigments synthesized from hematite. This is the result of higher magnetite reactivity and consequent creation of more fine products in which X-ray diffraction analysis failed to show the presence of alloy compounds. The core-shell ferrites were very effective in all the various environments where they were tested. The isometric particle pigments showed far more varied results in different environments. The difference in results also quite significant among particular coatings tested in the same chamber. Despite these facts, the results proved that isometric particle pigments improve the anticorrosion properties of the epoxyester coatings and are especially useful in an environment of NaCl and humidity [12].

5. Conclusion

The tested pigments showed high corrosion resistance. A comparison of all results proved that all synthesized pigments enhanced the anticorrosion effect of prepared coatings. Core-shell pigments showed the highest degree of anticorrosion efficiency. $Mg_{0,2}Zn_{0,8}Fe_2O_4$/Zn and $Ca_{0,2}Zn_{0,8}Fe_2O_4$/Zn showed the best results during testing. The anticorrosion properties of $ZnFe_2O_4$/Zn were also significant. Combining barrier protection, active anticorrosion protection (which is typical for ferrite and chemical protection given by partly oxidized zinc core) is the main advantage of this core-shell pigment. These core-shell ferrites show a complex mechanism, as they were very effective in all the various environments where they were tested.

Acknowledgements

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